

### Chapter 5 – Which Sections for the Exam?

**Chapter 5:** All sections except section 5.11 were covered. Section 11 is an interesting section on atmospheric chemistry but we will not cover it. Also sections 6-9 have lots of technical proofs that will NOT be on the exam. Let me point you to the KEY parts of those sections. Pages 154-155 very important... then skim all the way to page 160 and note the 2 boxed formulas, one for kinetic energy and the other for rms particle velocity. Then, on page 161 and 162, note the LOOK of a Maxwell-Boltzmann distribution and how the curve shifts with temperature (Figure 5.16). Know your definitions of effusion and diffusion plus the boxed equation at the bottom of page 162 (Graham's Law of Effusion). You can now skim again all the way to section 5.10 where you will READ carefully about real gases.

### Fundamentals

Know how to calculate molar mass. Know your nomenclature (still). Be able to calculate amounts of reactants or products when given amounts of reactant or products – this is called stoichiometry – KNOW IT. See chapters 1-3 Know how to determine the limiting reactant and how much product it leads to. Be able to incorporate percent yield into a problem if necessary. All that is new is moles to  $P$  or  $V$  instead of grams.

### How to measure pressure

Know the basics of how a manometer works and how a barometer works. Know how to calculate the pressure due to a standing column of liquid:

$$P = dgh \quad \text{or} \quad P = \rho gh$$

$d$  and  $\rho$  (rho) are density. Watch your units here.

Pressure will be in Pascals if you use  $\text{kg/m}^3$  for density, and  $m$  for height. If the column is mercury, just get the height in  $\text{mm}$  and you've now got torr.

### Gas Laws

Know the NAMES and the law associated with each name (scientist).

**Boyle's Law:** Pressure is inversely proportional to volume (assuming constant temperature and amount of gas, moles). Any units will work here.

$$P \propto 1/V \quad P_1V_1 = P_2V_2 = \text{constant}$$

**Charles' Law:** Volume is directly proportional to *absolute* temperature (assuming constant pressure and amount of gas, moles). Any units for volume but remember,  $T$  must be Kelvin.

$$V \propto T \quad \frac{V_1}{T_1} = \frac{V_2}{T_2} = \text{constant}$$

**Avogadro's Law:** Volume is directly proportional to amount of gas in moles. (assuming constant temperature and pressure).

$$V \propto n \quad \frac{V_1}{n_1} = \frac{V_2}{n_2} = \text{constant}$$

**Combined Gas Law:** Most books and people refer to this as Boyle's Law + Charles' Law which is

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad (\text{assuming constant } n)$$

However, our book throw's in Avogadro's Law also giving:

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} = \text{constant}$$

which is fine, except that this is really just the

**Ideal Gas Law** in disguise. The constant that is defined by this version of the combined gas law is the Universal Gas constant,  $R$ . So by definition:

$$R = \frac{PV}{nT} \quad \text{which rearranges to give}$$

$$PV = nRT$$

which is the **Ideal Gas Law** we all know and love.

When you use the ideal gas law be sure and use the right units on  $P$ ,  $V$ ,  $n$ , and  $T$ . You have no choice on  $n$  and  $T$ , they must be in moles and Kelvin. Now you've got choices for units on  $P$  and  $V$  and THAT's why we've got different values (OK, mostly different) of  $R$  listed in the book. Here are my favorites (feel free to find one as your favorite):

$$R = 0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \quad \text{the old trusty L}\cdot\text{atm one}$$

$$R = 8.314 \frac{\text{kPa}\cdot\text{L}}{\text{mol}\cdot\text{K}} \quad \text{or} \quad \frac{\text{Pa}\cdot\text{m}^3}{\text{mol}\cdot\text{K}} \quad \text{the SI unit one}$$

$$R = 62.36 \frac{\text{L}\cdot\text{torr}}{\text{mol}\cdot\text{K}} \quad \text{you gotta like torr}$$

You might notice that these all just differ by the unit factors for pressure conversions. Like

$$0.08206 \times 760 = 62.36$$

See, it's not so bad. But I know what you're thinking. Do I (state your name) need to memorize all those values of

R? Why not? Drop that value of  $R$  into your next conversation and watch your popularity skyrocket. Oh well, I will still print those values on the cover sheet to the exam for you to refer to while your brain is slowly melting during the exam.

## STP vs SATP

A standard is whatever you chose as standard. Sometimes we chose different standards – and yes, I think that defeats the point in the first place but there you go. Know the difference in STP and SATP:

STP: 0°C and 1 atm (old school, most of our problems)

SATP: 25°C and 1 bar (new school, newer problems)

Realize that you WILL need to convert °C into Kelvin.

## Let's MIX it up a bit

All those laws are great and work really well for most gases at reasonable pressures and temperatures. You can even apply those laws to mixtures of gases and just treat the whole mix as one big family of gas - that is you COUNT ALL the moles regardless of the type. When you do this you are calculating TOTAL pressure due to ALL the gases present. After you do that, I'm still going to want to know what the pressure is for each individual gas. The pressure exerted by say helium in a mixture of helium, neon, and xenon is the partial pressure of helium,  $P_{\text{He}}$ . Now the big lesson (and name!),

**Dalton's Law of Partial Pressures:** The total pressure of a system is equal to the sum of all the partial pressures within the system. Mathematically:

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

Now also realize that each of those partial pressures will have it's own version of the ideal gas law. What I mean is that  $P_A V = n_A RT$ . See, I'm only counting moles of A in this equation and I therefore get out  $P_A$ . One of the other neat results of this law is that the partial pressure's ratio to the total pressure exactly matches its mole fraction. Uh-oh, what's a mole fraction? The number of moles of A divided by the total moles of gas in the mixture. Mole fraction of A is given by the symbol  $x_A$  (OK, so it's  $\chi_A$  in the book – much too greek for me). So by definition:

$$x_A = \frac{\text{mol A}}{\text{mol A} + \text{mol B} + \text{mol C} + \dots}$$

and you can set that equal to the pressure ratios:

$$x_A = \frac{P_A}{P_{\text{total}}} \quad \text{and therefore} \quad P_A = x_A P_{\text{total}}$$

So you can use pressures to get mole fractions OR use mole fractions to get pressures. Cool.

## The confusion on effusion

Effusion of a gas is when a gas slips through a very small hole (or holes) from a high pressure to a low pressure. This IS what is going on when your once large and buoyant helium balloon (fun) is now much smaller and is now riding around on the floor (not as fun). Helium effuses through the pores of the latex balloon. How fast does the helium effuse? Graham knows.

**Graham's Law of Effusion:** At constant temperature, the rate of effusion of a gas is inversely proportional to the square root of its molar mass.

$$\text{rate of effusion} \propto 1/\sqrt{M}$$

and so if you compare two gases at the same temperature you'll get

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \sqrt{\frac{M_B}{M_A}}$$

The same exact relation works for average speed also.

Temperature has the same square root dependence, but it is directly proportional to the rate of effusion or speed. For a given molar mass at two different temperatures:

$$\frac{\text{rate of effusion (or speed) at } T_2}{\text{rate of effusion (or speed) at } T_1} = \sqrt{\frac{T_2}{T_1}}$$

You can now combine the two affects of mass and temperature and get

$$\text{rate of effusion (or speed)} \propto \sqrt{\frac{T}{M}}$$

This can be set to an equality with a little work. YOU, however do not need to worry about that work and just look at the final equation:

$$v_{\text{rms}} = \left( \frac{3RT}{M} \right)^{1/2} \quad (\text{bottom of page 160})$$

Where  $v_{\text{rms}}$  is the root mean square speed.

## You don't know how it feels – to be me

Ah yes, Tom Petty sang it so well and he never realized just how much all the real gases love that song. How DOES it feel to be real? Well for starters, you've got a real volume your OWN self. Real gas molecules DO have real diameters and take up space – ideal gases do NOT have a real diameter – they are just a point in space. Speaking of point, Tom Petty says in the same song, "let's get to the point..." See he was talking about ideal gases right? Actually, now that I think about it, and sing the rest of that chorus... he's talking about a whole other gas. But WAIT! Yes, he IS talking about real gases now that I think about it! Another line, "... think of me what you will, I've got a little space to fill". SEE? That's what gases do – fill space. I digress.

A great way to show non-ideality is to calculate a gas's actual (real) molar volume,  $V_m$ , and compare it to the molar volume of an ideal gas,  $V_m^{\text{ideal}}$ . When compared as a ratio, you get the **compression factor,  $Z$** .

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}} \text{ which also equals } \frac{PV_{\text{real}}}{nRT} \text{ which}$$

is plotted vs pressure in your book on page 170 in Figure 5.22. Your book doesn't call it  $Z$  but that is what it is. An ideal gas will have  $Z = 1$  under ALL conditions. Real gases have real forces at play. A value of  $Z < 1$  corresponds to attractive forces being dominant. A value of  $Z > 1$  corresponds to repulsive forces being dominant. Note that as zero pressure is approached, all real gases take on ideal behavior ( $Z = 1$ ). Real gases aren't that far off the line at 1 atm either, which is why the ideal gas law works so well most of the time.

### How to improve on an already IDEAL equation?

It is possible to come up with an equation that attempts to include the effects of attractions and repulsions between the gas particles. It does not predict the exact behavior of a real gas, but it comes closer. The main problem is that you must PICK the real gas you want the "law" to work for. All gases are NOT the same in the real world of gases, especially at high pressures and low temperatures – that is where the ideal gas law is at its worst.

#### The van der Waals equation:

$$\left( P + a \frac{n^2}{V^2} \right) (V - nb) = nRT$$

Now we've got a fixed up equation that has added two new parameters. One to deal with attractions ( $a$ ), and one to deal with repulsions ( $b$ ). These are the van der Waals parameters and they are NOT temperature dependent – yea! You DO need to look up the values for  $a$  and  $b$  for every gas you want to work with though. The parameter  $a$  is an "adjustment" for attractive forces between molecules. The bigger  $a$  is, the smaller the pressure will be. The parameter  $b$  is like a volume correction term – it is roughly the volume of a mole of condensed gas. It essentially accounts for the repulsions between the gas particles.

### Life's a Gas – now you know more about it.

Yes, read your book. Try some of those problems in the back of the chapter. You'll feel so GOOD about yourself.

#### Standard Disclaimer

Any mistakes on this review sheet are NOT intentional. You should crosscheck all stated information. You should double check your book too (see errata).